Journal of Power Sources 249 (2014) 79–83

Contents lists available at ScienceDirect

Journal of Power Sources

journal homepage: www.elsevier.com/locate/jpowsour

Short communication

Micro-solid oxide fuel cell supported on a porous metallic Ni/stainless-steel bi-layer

Younki Lee [a], Young Min Park [b], Gyeong Man Choi [a,*]

[a] Fuel Cell Research Center/Department of Materials Science and Engineering, Pohang University of Science and Technology (POSTECH), Pohang 790-784, Republic of Korea

[b] Fuel Cell Project, Research Institute of Industrial Science and Technology (RIST), Pohang 790-330, Republic of Korea

HIGHLIGHTS

- A new design was created for the fabrication of micro-solid oxide fuel cell.
- Ni and stainless-steel were used as a strong and porous metallic-support.
- The cell showed stable Ohmic resistance at 450 °C after operation for 112 h.

ARTICLE INFO

Article history:
Received 3 September 2013
Received in revised form
16 October 2013
Accepted 17 October 2013
Available online 25 October 2013

Keywords:
Micro-solid oxide fuel cells
Stainless steel
Metal supports
Thin films

ABSTRACT

Metallic bi-layer of porous Ni and porous stainless steel (STS) is utilized as a support for micro-solid oxide fuel cells (SOFCs) using a thin-film layer of electrolyte. Tape-casting and screen-printing processes are employed to fabricate a thick (~250 μm) STS-layer covered with a thin (~20 μm) nano-porous Ni layer. Successful deposition of a nearly pore-free electrolyte layer by the pulsed laser deposition (PLD) method is demonstrated by the high open-circuit-voltage (OCV) value of a single cell. The Ohmic resistance of the micro-SOFC deposited on a porous Ni/STS-support is stable and it shows ~28 mW cm^{-2} after operation for ~112 h at 450 °C. The use of a porous Ni/STS bi-layer as a support for micro-SOFCs is successfully demonstrated.

1. Introduction

Micro-solid oxide fuel cells (micro-SOFCs) are considered as promising power sources for portable devices since high specific energy and energy density can be obtained if the cell is successfully fabricated [1]. Conventional SOFCs require high operating temperatures (800–1000 °C) due to the advantages of fast ionic transport in cell components and direct utilization of hydrocarbon fuels without pre-reforming [2]. Since high operating temperature is a barrier for integration of micro-SOFCs into small electronics, operation at low temperature (<500 °C) and miniaturization of the cell components are required including reduction of the electrolyte thickness [1,3–9].

Micro-SOFCs use thin-film components including electrolyte and electrodes, which are supported on a porous substrate. The support for micro-SOFCs requires high mechanical strength, porosity for the diffusion of fuel gas, and a smooth surface for the deposition of a thin and dense electrolyte layer. Pulsed laser deposition (PLD) or RF magnetron sputtering methods are often used to deposit thin-film cell components on a substrate or support. Conventional substrates such as a Si wafer can be used but additional lithography and etching processes are complicated and mandatory to provide gas paths [3–5]. The active area of the cell is also restricted to a micrometer-scale due to the processing difficulties [6]. Although lithography and etching processes are still required, glass-ceramic was also used as a support for micro-SOFCs due to its similar thermal expansion coefficient (TEC, 8.6–10.5 × 10^{-6} K^{-1}) to electrolyte materials such as yttria-stabilized zirconia (YSZ, 10.5 × 10^{-6} K^{-1}) and gadolinium-doped ceria (GDC, 12.4 × 10^{-6} K^{-1}) [6,10,11]. In order to avoid complex lithography and etching processes, porous substrates such as porous Ni and anodized alumina are also used as a support [6–9].

Although an electrolyte in the form of a thin film has the advantages of reduced Ohmic resistance, structural instability of the

* Corresponding author. Tel.: +82 54 279 2146; fax: +82 54 279 2399.
E-mail address: gmchoi@postech.ac.kr (G.M. Choi).

0378-7753/$ – see front matter
http://dx.doi.org/10.1016/j.jpowsour.2013.10.082

film, e.g. buckling failure or delamination, has been reported [6,12,13]. These results may be due to thermal stress originating from the mismatch of the TECs between the thin-film electrolyte and the support.

A ferritic stainless steel (STS) is generally used as an interconnect material and is also regarded as a promising support material due to its similar TEC ($\sim 11.5 \times 10^{-6}$ K^{-1}) with YSZ and GDC electrolytes and its good oxidation resistance at intermediate temperature (500–800 °C) [14]. In addition, metallic supports have advantages for SOFCs such as high electrical conductivity and high mechanical strength. However, a micro-SOFC using an STS-support has not been reported. This might be due to the difficulty of designing a porous structure of STS. Lithography, selective etching process or conventional powder metallurgy process are not suitable for the fabrication of pores on a sub-micrometer scale in STS.

In this study, a bi-layer composed of a nano-porous Ni layer coated on a macro-porous STS was fabricated for use as a metal support. A nano-porous Ni layer is more suitable as a support than a macro-porous STS since a dense thin film can only be deposited on the surface of a nano-porous substrate. However, its high TEC ($\sim 16.5 \times 10^{-6}$ K^{-1}, 435 °C) is a problem due to the mismatch with the electrolyte layer and subsequent delamination of the Ni layer from the electrolyte layer [6]. This problem may be alleviated by attaching a thick STS layer with a TEC similar to that of the electrolyte, to the thin Ni layer with a high TEC. In addition, the Ni/STS bi-layer can be fabricated by employing simple tape-casting and screen-printing processes that do not require complex lithography and etching processes. In this study, a single cell of a micro-SOFC was deposited on a metallic bi-layer and its electrochemical properties were evaluated at 450 °C. 1 mol% Ga_2O_3–added $Gd_{0.2}Ce_{0.8}O_{2-\delta}$ (hereafter GDC-1Ga or GDC) and 8 mol% yttria-stabilized zirconia (YSZ) thin films were employed as a bi-layered electrolyte. Delamination due to weak adhesion between the porous Ni support layer and the GDC electrolyte was avoided by positioning a Ni-GDC anode layer between them.

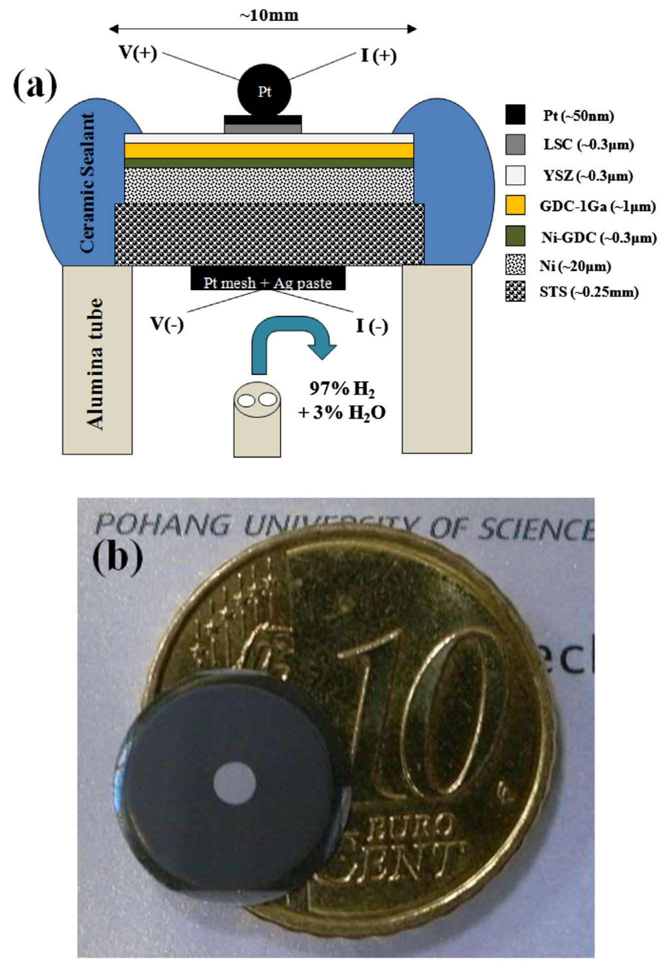

Fig. 1. (a) Schematic illustration and (b) photograph of a micro-SOFC supported on a Ni/STS bi-layer support.

2. Experimental

A schematic illustration of a single cell of micro-SOFC is shown in Fig. 1a, supported on Ni/STS. The thicknesses of cell components are also shown. In order to form a porous metallic support, a STS green-sheet was fabricated by a tape casting method by using commercial STS-434L powders (d_{50} ~10 μm, Daekwang Industry, Korea). Slurries were prepared by mixing the STS powders, 15 wt% starch powders (D.C. Chemicals, Korea), and a polymeric solution containing toluene, ethanol, polyvinyl butyral (PVB, B-74), and dioctyl phthalate as a solvent, a binder, and a plasticizer, respectively. The green sheet was fired at 1150 °C for 3 h in a dry hydrogen atmosphere. After firing, the porous STS sheet was punched out to produce metal sheets of 10 mm diameter and 0.25 mm thickness. The surface of the STS sheet was rough on a micro-meter scale due to large STS particles and thus the sheet was subsequently flattened by uniaxial pressing and polishing. Ni-paste (Samsung Electro-Mechanics, Korea), a mixture of Ni nano-particles and a polymeric solution, was screen-printed onto the pre-fired STS substrate and fired at 575 °C in dry hydrogen for 3 h.

The NiO–GDC (NiO–$Gd_{0.2}Ce_{0.8}O_{2-\delta}$) layer was deposited on the surface of the nano-porous Ni layer via PLD process. To prepare a target, NiO (High Purity Chemicals, 99.9%, Japan) and GDC (Fuel Cell Materials, M Grade, USA) were mixed with a 6:4 ratio in weight, uniaxially pressed to form a pellet, and sintered at 1400 °C for 5 h in air. The base pressure for the thin film deposition was 8×10^{-4} Pa and PLD was performed for 1 h with a KrF-excimer laser (248 nm) at ~120 mJ $pulse^{-1}$ energy and a 10 Hz repetition rate in oxygen pressure of 6.7 Pa. The substrate was held at 600 °C. The GDC and YSZ thin films were sequentially deposited as a bi-layer electrolyte by using similar deposition conditions except for oxygen pressure of 4.0 Pa and deposition time of 1.1 h and 1 h, respectively. In order to fabricate GDC and YSZ targets, commercial GDC powder (Fuel Cell Materials, M Grade, USA) with the addition of 1 mol% of Ga_2O_3 (High Purity Chemicals, 99.9%, Japan) and an YSZ powder (TZ-8YS, Tosoh, Japan) were cold-isostatically pressed, and subsequently sintered at 1550 °C for 4 h, respectively. The addition of 1 mol% Ga_2O_3 into GDC was previously shown to be advantageous for densification of a GDC film [15]. A $La_{0.7}Sr_{0.3}CoO_{3-\delta}$ (LSC) layer was also deposited on the YSZ electrolyte by PLD at room temperature for 1.2 h under oxygen pressure of 2.7 Pa. The area of the LSC cathode was ~3.1 mm^2. The same energy and repetition rate were used. The LSC powder was pressed and sintered at 1000 °C for 2 h to produce a target. Pt was deposited on the LSC cathode with a DC coater. The base pressure was ~10 Pa and current of 25 mA was applied for 240 s. Pt bead (d ~ 1 mm) was used as a current collector at the cathode side. For current collection at the fuel side, a Pt mesh and Pt wires were attached by using an Ag-paste.

The fabricated micro-SOFC with a metal support was then mounted on an alumina tube with a ceramic sealant for evaluation at 450 °C by flowing wet hydrogen gas as fuel and using stationary air as an oxidant. The flow rate of the fuel gas was ~70 cm^3 min^{-1}. Both heating and cooling rates were 1 °C min^{-1} and the cell dwelled at 90 °C for 2 h to cure the sealant. Cell voltage and temperature were measured with a programmable electrometer (Model 617, Keithley, USA) and a thermometer (Model 740,

Keithley, USA), respectively. The impedance spectra were obtained in the frequency range of 1 Hz–5 MHz using an impedance analyzer (SI 1260, Solartron, UK). *I* (current density)–*V* (voltage)–*P* (power density) curves were obtained with an electrochemical interface (VSP, Biologics, France). The microstructure of the cell was examined with field-emission scanning-electron microscopes (FE-S.E.M., JEOL, model 3330F and 7401F, Japan).

3. Results and discussion

3.1. Physical characterization

Fig. 1b is a photograph of a micro-SOFC supported on Ni/STS bi-layer with a diameter of ~10 mm. The fabricated cell was strong enough for easy handling by hand. The area of the electrolyte was ~0.7 cm^2 with this design, which is 10–1000 times larger than that of previous micro-SOFCs using a porous Ni support [7] or a glass-ceramic support [10]. This may be attributable to the high mechanical strength of the Ni/STS layer and because the TEC-mismatch between the ceramic components and the Ni substrate is partially reduced by the underlying STS layer.

A SEM image (top view) of porous STS, tape-casted with commercial STS-434L powder and then fired at 1150 °C for 3 h in a reducing atmosphere, is shown in Fig. 2a. Porosity of the support

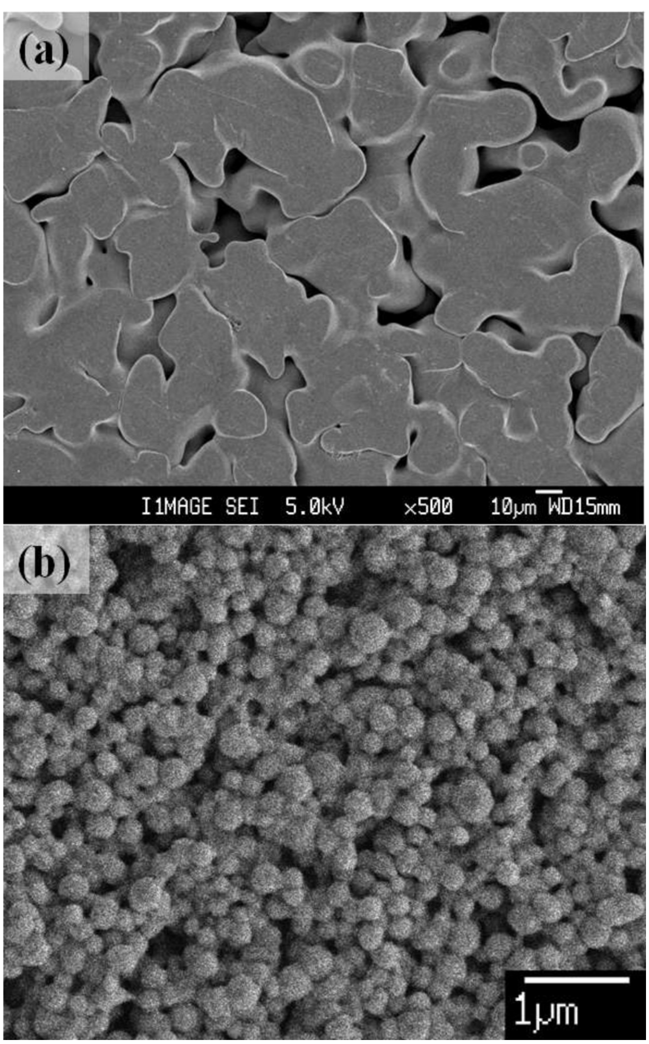

Fig. 2. S.E.M. images of porous metals fired in reducing atmosphere; (a) STS fired at 1150 °C, and (b) Ni fired at 575 °C.

was estimated as ~40% by simple calculation with mass and dimensions of the metal sheet. Both the grain and pore sizes of the STS layer were larger than the size (~10 μm) of the starting metal powders. The grain and pore sizes of the Ni layer were 150–450 nm and <300 nm, respectively (Fig. 2b). According to our experience, in order to obtain a dense electrolyte layer by PLD, the thickness of the electrolyte layer should be at least 2–3 times larger than the pore size in a porous substrate. Thus, the thickness of the electrolyte layer deposited on the porous Ni layer should exceed roughly ~1 μm in this study.

Fig. 3a shows a cross-sectional SEM image of the micro-SOFC in this study after an electrochemical test operated for longer than 100 h. The STS-support with thickness of ~0.25 mm is not shown in the image at this magnification. Cell components including a Pt current collection layer, an LSC cathode, an YSZ/GDC bi-layer electrolyte, and a Ni–GDC anode are shown on the Ni/STS metal support. The thickness of the cathode is ~300 nm. An YSZ (t ~ 0.3 μm) layer was deposited on top of the GDC (t ~ 1.3 μm) layer to prevent oxygen permeation and subsequent reduction of the cell voltage due to the electronic conduction of the GDC electrolyte [6,8]. Bi-layer of relatively thin YSZ and thick GDC layers was used to minimize the Ohmic resistance of the cell since the electrical conductivity of GDC is higher than that of YSZ. Although both layers show a columnar microstructure, structural defects such as cracks and cleavages were rarely observed in this image. Since YSZ is known as a nearly pure-ionic conductor even in a fuel atmosphere, the open circuit voltage (OCV) of the cell using a dense YSZ electrolyte is expected to be close to the Nernst voltage [3]. The nano-porous anode layer of Ni–GDC is shown in high magnification (Fig. 3b). Although weak adhesion between GDC and Ni was shown [6], the existence of the ~0.3 μm-thick Ni–GDC layer may have improved the adhesion between the two layers, judging from the stable electrochemical performance shown later. The improved adhesion can possibly be ascribed to the composition and the thermal expansion coefficient of the Ni–GDC composite being intermediate between those of GDC and Ni.

3.2. Electrochemical analysis

3.2.1. Electrochemical impedance spectra

Fig. 4 shows impedance spectra of the fabricated cell measured at 450 °C during operation for 43 h–112 h under an open-circuit condition. A large decrease in the size of the semicircle was shown from 43 h to 112 h. The performance was stabilized after 100 h. The area-specific Ohmic resistance (R_{ohm}), determined from the intercept of a high-frequency arc with the real axis, shows little change. The change was due mostly to the decrease in the area-specific polarization resistance (R_P) with time. The R_{ohm} values show a slight fluctuation between 0.29 and 0.36 Ω cm^2 with time; however, they were close to the estimated value (~0.25 Ω cm^2) using the dimensions of the YSZ and GDC films and the reported electrical conductivities of bulk YSZ and GDC [15,16]. The results imply that no significant delamination between the layers occurred during ~100 h. The R_P value decreased slowly with time and was nearly saturated after ~100 h. The slow change is not clearly understood at present; it might be due to the slow kinetics of reducing the anode layer. Low operating temperature and slow gas flow through nano-porous channels in the anode may be responsible for the slow reduction of NiO. The R_P value of ~3.8 Ω cm^2 after 112 h is comparable to the R_P value (~3.4 Ω cm^2) reported in the literature for a micro-SOFC supported on porous Ni, an LSC/GDC/Ni cell [7]. However, it is ~20 times smaller than that of a micro-SOFC supported on a glass-ceramic substrate (a $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ (LSCF)/YSZ/sputtered Pt cell) at the same temperature [10].

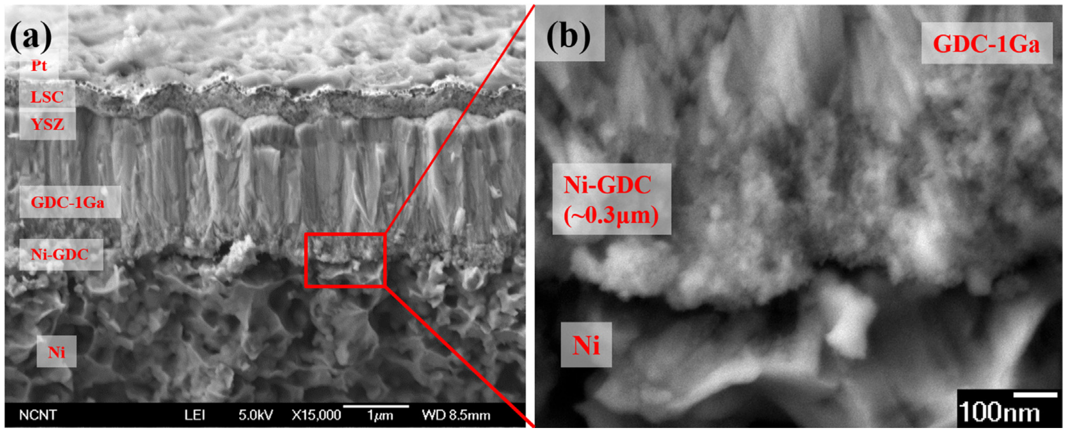

Fig. 3. Cross-sectional S.E.M. images of (a) a micro-SOFC supported on a Ni/STS bi-layer (Pt/LSC/YSZ/GDC/Ni–GDC/Ni), (b) magnified view of the cell near anode layer (GDC/Ni–GDC/Ni).

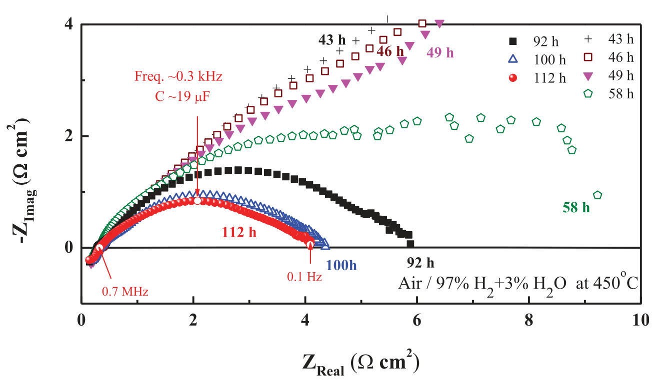

Fig. 4. Impedance spectra of a micro-SOFC supported on a Ni/STS bi-layer in an open circuit condition as a function of time (43 h–112 h) at 450 °C. Frequencies and the capacitance value are shown for the impedance spectra obtained after 112 h.

3.2.2. I–V–P curves

Fig. 5 shows *I* (current density)–*V* (cell voltage)–*P* (power density) curves of the present single cell at 450 °C after 46 h–112 h. The OCV value increased for 112 h before it was stabilized. The slow OCV increase is clearly associated with the slow decrease of R_P values, originating from the insufficient local gas-exchange and thus slow reduction of NiO at the anode at low temperature. OCV of ∼0.91 V was shown after 112 h and is comparable to the reported OCV values of micro-SOFCs using an YSZ electrolyte; Kerman et al. reported values of 0.8–1.0 V at ∼450 °C with an active area of 0.03 mm^2 (Pt/YSZ/Pt on a Si substrate) [4] and Tsuchiya et al. reported a value of ∼0.77 V at 451 °C with an active area of 13.5 mm^2 (LSCF/YSZ/Pt on a Si-substrate) [5].

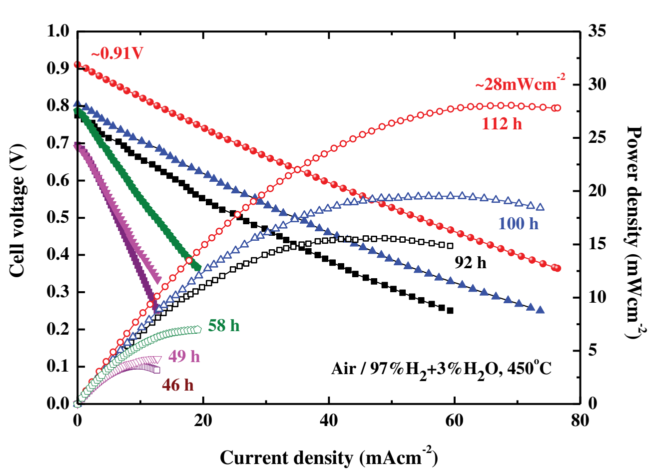

Fig. 5. *I* (current density)–*V* (voltage)–*P* (power density) curves of a micro-SOFC supported on Ni/STS were obtained at 450 °C for 46 h–112 h. Wet hydrogen gas and stationary air were used as fuel and oxidant gases, respectively.

The reason for the low OCVs compared to the Nernst potential (∼1.18 V) in this study is unclear at present. Tsuchiya et al. proposed that gas leakage through defects on the sealant was the cause of decreased values [5]. The relatively high OCV of ∼0.91 V was obtained in this study since no obvious cracks were observed on the surface of YSZ electrolyte of the cell, as shown in SEM micrographs after the electrochemical test. Furthermore, the observed leakage (∼2 cm^3 min^{-1}) due to insufficient sealing was small compared to the flow rate of H_2 gas (70 cm^3 min^{-1}) during this experiment. Muecke et al. also obtained OCVs of 0.4–0.9 V at 400–600 °C for the YSZ-cells fabricated by etching glass-ceramic supports, and they attributed the low OCV values to gas leakage resulting from the columnar structure of the YSZ electrolyte layer [10].

The maximum power density (MPD) of the cell was gradually increased with operation time and it showed ∼28 mW cm^{-2} at 450 °C after 112 h. The value was in the same range as several reported values; Joo and Choi reported a value of ∼26 mW cm^{-2} at 450 °C with an LSC/GDC (t ∼ 3 μm)/Ni-support cell [6]. Muecke et al. achieved ∼17 mW cm^{-2} at 450 °C with a Pt/YSZ bi-layer/Pt cell supported on a glass-ceramic substrate [10]. The power density of the present cell will further be increased by reducing R_P values through optimization of the microstructure of cell components, especially that of the cathode and anode. The present micro-SOFC using a Ni/STS bilayer-support has successfully operated for 112 h with high OCV and a reasonable value of power density. To the best of our knowledge, this is the longest successful operation of a micro-SOFC possibly due to the metallic bi-layer support. The simple fabrication method reported here is also a notable advantage.

4. Conclusions

Metallic bi-layer composed of porous Ni and porous stainless steel (STS) was tested as a support for micro-solid oxide fuel cells. Simple tape-casting and screen printing processes were employed to fabricate a thick (t ∼ 250 μm) STS layer with large pores covered with a thin (t ∼ 20 μm) nano-porous Ni layer. Although thin layers

of GDC and YSZ electrolytes, sequentially deposited by the PLD method on a metallic bi-layer, displayed a columnar microstructure, they are nearly gas-tight and show a high value (0.91 V) of open circuit voltage. The electrochemical test of a single cell supported on a porous Ni/STS bi-layer showed the MPD of $\sim$28 mW cm^{-2} at 450 °C after operation for 112 h. The low and stable Ohmic resistance value also demonstrates that there was little development of delamination between the cell components with time. The use of a porous Ni/STS metallic bi-layer as a support for a micro-SOFC was thus successfully demonstrated. The simple fabrication method reported here is also an important advantage. The performance of the cell will further be increased by reducing the polarization resistance values through optimization of the microstructure of the anode and cathode.

Acknowledgments

This research was supported by Basic Science Research Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Education, Science and Technology (2011-0023389).

References

[1] A. Evans, A. Bieberle-Hütter, J.L.M. Rupp, L.J. Gauckler, J. Power Sources 194 (2009) 119–129.
[2] B.C.H. Steele, A. Heinzel, Nature 414 (2001) 345–352.
[3] H. Huang, M. Nakamura, P. Su, R. Fasching, Y. Saito, F.B. Prinz, J. Electrochem. Soc. 154 (2007) B20–B24.
[4] K. Kerman, B.-K. Lai, S. Ramanathan, J. Power Sources 196 (2011) 2608–2614.
[5] M. Tsuchiya, B.K. Lai, S. Ramanathan, Nat. Nanotechnol. 6 (2011) 282–286.
[6] Y. Lee, G.M. Choi, J. Electroceram. 31 (2013) 238–244.
[7] J.H. Joo, G.M. Choi, J. Power Sources 182 (2008) 589–593.
[8] J.H. Joo, G.M. Choi, Solid State Ionics 178 (2007) 1602–1607.
[9] C.-W. Kwon, J.-I. Lee, K.-B. Kim, H.-W. Lee, J.-H. Lee, J.-W. Son, J. Power Sources 210 (2012) 178–183.
[10] U.P. Muecke, D. Beckel, A. Bernard, A. Bieberle-Hütter, S. Graf, A. Infortuna, P. Müller, J.L.M. Rupp, J. Schneider, L.J. Gauckler, Adv. Funct. Mater. 18 (2008) 3158–3168.
[11] H. Hayashi, M. Kanoh, C.J. Quan, H. Inaba, S. Wang, M. Dokiya, H. Tagawa, Solid State Ionics 132 (2000) 227–233.
[12] C.D. Baertsch, K.F. Jensen, J.L. Hertz, H.L. Tuller, S.T. Vengallatore, S.M. Spearing, M.A. Schmidt, J. Mater. Res. 19 (2004) 2604–2615.
[13] K. Kerman, B.-K. Lai, S. Ramanathan, J. Power Sources 202 (2012) 120–125.
[14] S. Molin, M. Gazda, P. Jasinski, Solid State Ionics 181 (2010) 1214–1220.
[15] Y. Lee, J.H. Joo, G.M. Choi, Solid State Ionics 249–250 (2013) 165–170.
[16] J.H. Joo, G.M. Choi, J. Eur. Ceram. Soc. 27 (2007) 4273–4277.